17

THE CRYSTAL STRUCTURES OF METALLIC FLUOBERYLLATES, DOUBLE FLUOBERYLLATES AND SULPHATO-FLUOBERYLLATES

By P. L. MUKHERJEE

(*Received for publication, 13th May, 1944*)

(Plates II*a* and II*b*)

ABSTRACT. Crystals of the fluoberyllates of Rubidium, thallium, potassium and ammonium have been studied goniometrically and by X-rays. It has been found that these crystals are isomorphous among themselves as well as with the crystals of the sulphates of the corresponding metals, both as regards crystal class and axial lengths. The space group of the crystals of the potassium compound has been determined and found to be identical with that of potassium sulphate. Crystals of the double fluoberyllates (*a*) $Zn(NH_4)_2(BeF_4)_2, 6H_2O$ (*b*) $Co(NH_4)_2(BeF_4)_2, 6H_2O$ and (*c*) $Ni(NH_4)_2(BeF_4)_2, 6H_2O$ and also of the substance $NiK_2BeF_4, SO_4, 6H_2O$ are isomorphous among themselves as well with the sulphates. The axial lengths of $Ni(NH_4)_2(BeF_4), 6H_2O$ have been measured and found identical with those of corresponding double sulphate.

INTRODUCTION

Works of Sarkar and Roy (1929) on the Fluoberyllates furnished quite a new example of a homologous radical in BeF_4 of the radical SO_4. They actually observed that many simple and complex salts (including alums) of these two ions are perfectly isomorphous—their respective solubilities and molecular volumes are also very close, and even the organic salts of the corresponding acids are physically and chemically similar. They further found the crystals of a fluoberyllate to grow uniformly well in a saturated solution of the corresponding sulphate.

It is a well-established fact in crystallography, which has been corroborated by X-ray evidence, that chemically and physically isomorphous selenates and sulphates are also isomorphous crystallographically and structurally [Koch Holm and Schonfeld (1926)]. In the light of this result the author was led to investigate whether the chemical analogy of the fluoberyllates and sulphates as discovered by Sarkar and Roy can be pushed further so as to establish a real crystallographic and structural isomorphism among these substances too.

Three types of fluoberyllates taken up for investigation were :—

(1) Simple fluoberyllates—

(*a*) Rb_2BeF_4; (*b*) Tl_2BeF_4; (*c*) K_2BeF_4; (*d*) $(NH_4)_2BeF_4$.

(2) Double fluoberyllates—

(*a*) $Zn(NH_4)_2(BeF_4)_2, 6H_2O$;

(*b*) $Co(NH_4)_2(BeF_4)_2, 6H_2O$;

(*c*) $Ni(NH_4)_2(BeF_4)_2, 6H_2O$.

(3) Sulphato fluoberyllates—

(*a*) $Zn(NH_4)_2BeF_4.SO_4, 6H_2O$;

(*b*) $NiK_2BeF_4.SO_4, 6H_2O$.

GONIOMETRIC MEASUREMENTS

Goniometric measurements of the crystals of these salts were carried out by means of a Fuess two-circle goniometer.

(1) *Simple Fluoberyllates*—

(*a*) Rubidium fluoberyllate Rb_2BeF_4.

Class.—Orthorhombic bi-pyramidal.

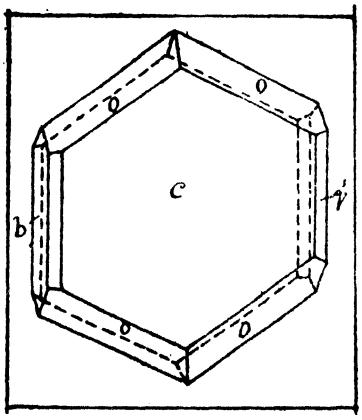
Preparation.—The salt was prepared by double decomposition of $(NH_4)_2BeF_4$ and $RbNO_3$. Crystals are easily obtainable from saturated aqueous solution of the salt at ordinary temperatures. These crystals possess a very high tendency to get twinned.

Habit.—The substance forms transparent crystals with a large growth in the directions of '*a*' and '*b*' axes. They occur as thin plates of c (001) faces bounded by the faces b (010), k (021), o (111) and occasionally q (011). (Fig. 1).

Specific gravity = 3.243.

Axial ratios of Rb_2BeF_4 $a:b:c = 0.5766:1:0.7560$.

Axial ratios of Rb_2SO_4 $a:b:c = 0.5723:1:0.7485$.



Rb_2BeF_4

FIG. 1

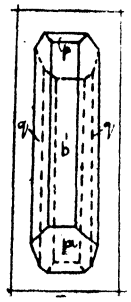
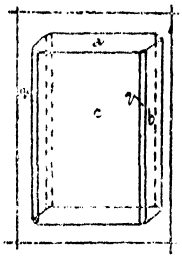


FIG. 2(*a*)



Tl_2BeF_4

FIG. 2(*b*)

—	—	Observed	Calculated	Corresponding sulphate
001	021	56°34′	56°31′	56°15′
010	021	33°37′	33°30′	33°45′
001	111	56°21′	56°31′	56°26′
021	111	49°10′	49°19′	49°22′
010	111	65°26′	65°22′	—
$\bar{1}11$	111	49°1′	49°8′	48°54′
011	111	46°10′	46°17′	—

(*b*) Thallium fluoberyllate Tl_2BeF_4.

Class.—Orthorhombic bipyramidal.

Preparation.—The substance was prepared by double decomposition of thallium nitrate and ammonium fluoberyllate.

The crystals were easily obtained as slightly transparent needles from saturated solution of the substance in water at ordinary temperatures. These crystals possess a very great tendency to become twinned though the faces of each component of a twinned crystal are generally quite perfect.

Habit.—The crystals are mostly very narrow elongated needles consisting of faces b (010), c (001) and limited by a top face a (100) ; when these needles are a bit thicker, the faces q (011) also appear [Fig. 2(*a*)]. Needles are also seen with a single top face m (110) or n (130) instead of a (100). Elongated thin plates of faces c (001) bounded by b (010) and a (100) are also found to occur occasionally. [Fig. 2(*b*)].

Specific gravity = 6.650.

Axial ratios of Tl_2BeF_4 $a:b:c = 0.5638:1:0.7368$.

Axial ratios of Tl_2SO_4 $a:b:c = 0.5555:1:0.7328$.

—	—	Observed	Calculated	Corresponding sulphate
010	130	30°31′	30°36′	30°58′
010	011	53°37′	53°37′	53°46′
010	110	60°38′	60°35′	60°57′

(*c*) Potassium fluoberyllate K_2BeF_4.

Class.—Orthorhombic bipyramidal.

Preparation.—The salt was prepared by digesting beryllium carbonate in a solution of potassium bifluoride. The substance being very much less soluble in water comes down immediately. After purification by recrystallisation single crystals are finally obtained from a saturated aqueous solution.

Habit.—Crystalline habits of the substance are (1) very short prism with faces (010), (001) with an additional face (021) and with end faces (111), (110). Fig. 3(*a*).

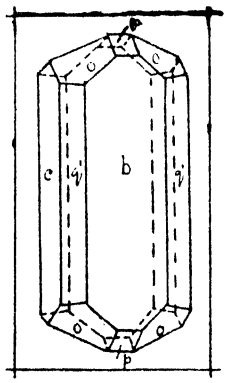


FIG. 3(*a*)

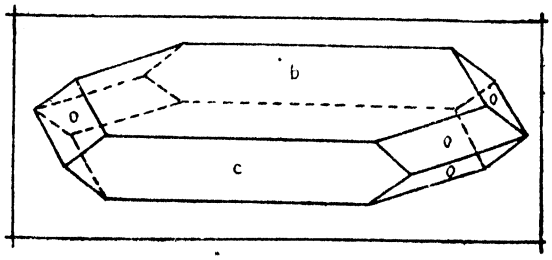


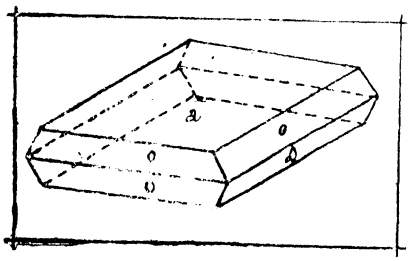
FIG. 3(*b*)

(2) Thick plates (010) bounded by the faces (001) and (111) (the most common type). Fig. 3(*b*).

(3) Thin plates (100) bounded by faces (111) occurring very rarely. Fig. 3(*c*).

(4) Needles with faces (010), (001), (021) limited by faces (111). Fig. 3(*d*).

Specific gravity = 2.649.



K_2BeF_4

FIG. 3(*c*)

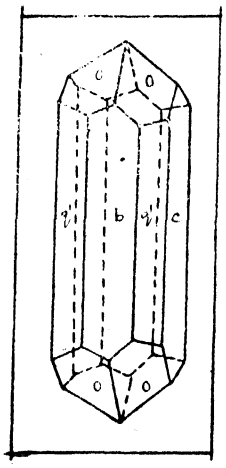


FIG. 3(*d*)

This crystal has been goniometrically studied by Marignac. His data has been confirmed by our measurements. The data for this substance given below are Marignac's data quoted from Groth's Chemische Krist. Vol. I, p. 342.

Axial ratios of K_2BeF_4 $a:b:c = 0.5708:1:0.7395$.

Axial ratios of K_2SO_4 $a:b:c = 0.5727:1:0.7418$.

—	—	Observed	Calculated	Corresponding sulphate
110	$1\bar{1}0$	59°26′	59°26′	—
111	$\bar{1}11$	48°40′	48°38′	48°46′
111	$1\bar{1}\bar{1}$	88°20′	87°39′	—
112	$\bar{1}12$	34°50′	34°29′	—
112	$1\bar{1}2$	62°10′	62°34′	—
001	021	56°0′	55°56′	56°1′
001	$\bar{1}11$	56°10′	56°10′	—
021	$\bar{1}11$	49°10′	49°14′	49°12
021	$\bar{1}12$	45°48′	46°1′	—

(*d*) Ammonium fluoberyllate $(NH_4)_2BeF_4$.

Class.—Orthorhombic bipyramidal.

Preparation.—The substance was obtained by decomposing beryllium carbonate with ammonium bifluoride.

Crystallisation.—It is very difficult to get suitable single crystals. The aqueous solution becomes highly supersaturated and then suddenly gives out a crop of transparent crystals which are abnormally twinned.

Habit.—The crystal forms long needles of faces (001), (010), (011) limited either by one pair of (100) faces or two pairs of (110) faces of which one is much larger than the other. The (001) face is always much broader than the (010) face and this broadening often becomes so prominent as to give rise to thin narrow plate-like types.

Specific gravity = 1.683.

The crystal has also been studied by Marignac whiose measurements have been confirmed by us. The data given below are from Groth's Chemische Krist. Vol. 1 p. 342.

Axial ratios of $(NH_4)_2BeF_4$ $a : b : c = 0.5655 : 1 : 0.7367$.

Axial ratios of $(NH_4)_2SO_4$ $a : b : c = 0.5635 : 1 : 0.7319$ $(NH_4)_2BeF_4$.

—	—	Observed	Calculated	Corresponding sulphate
010	110	60°30′	60°22′	60°41′
111	111	48°16′	48°28′	
001	021	55°50′	55°50′	55°40′
001	111	56°5′	56°8′	
111	011	46°12′	46°12′	
111	021	49°13′	49°16′	
110	021	66°2′	65°51′	

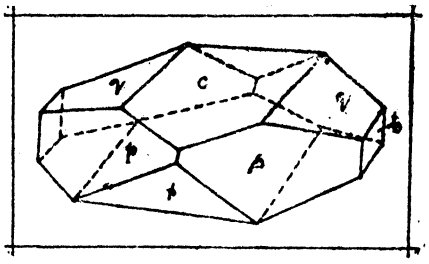
(2) *Double Fluoberyllates*—

(a) *Zinc Ammonium Flouberyllate*

$$Zn(NH_4)_2(BeF_4)_2,\ 6H_2O.$$

Class.—Monoclinic prismatic.

Preparation.—Zinc fluoberyllate is prepared by double decomposition of zinc chloride and thallium fluoberyllate and zinc fluoberyllate mixed with requisite amount of $(NH_4)_2BeF_4$. Crystallisation of this substance is difficult. Aqueous solution becomes highly supersaturated forming a syrupy liquid. The solution, however, gives very beautiful colourless transparent crystals when crystallisation is induced by throwing a crystal of zinc ammonium sulphate.



$Am_2Zn(BeF_4)_2,\ 6H_2O$

FIG. 4

Habit.—These crystals commonly occur as large thick plates of faces c(001), q(011), s(20$\bar{1}$) and o(111) which are not so prominent [Fig. 4]. The prismatic type is also met with frequently.

Specific gravity = 1.859.

Axial ratios $a : b : c = 0.7387 : 1 : 0.4909$; $\beta = 106° 34'$.

—	—	Observed	Calculated	Corresponding sulphate
110	110	70°33′	70°36′	70°26′
110	010	54°41′	54°42′	54°47′
110	011	62°50′	62°52′	62°27′
110	011	88°0′	88°0′	88°0′
110	201	53°1′	53°3′	52°34′
110	111	88°13′	88°3′	87°36′
110	001	76°33′	76°33′	76°17′
001	201	64°1′	64°1′	64°56′
001	011	25°11′	25°12′	25°33′
001	111	44°14′	44°13′	45°5′

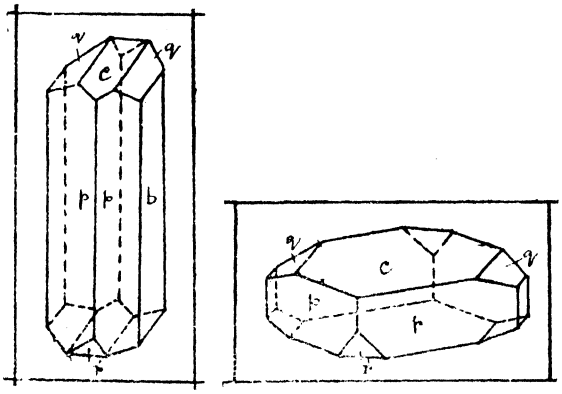
(*b*) *Cobalt Ammonium Fluoberyllate*

$Co(NH_4)_2(BeF_4)_2, 6H_2O$.

Class.—Monoclinic prismatic.

Preparation.—The method of preparation was very similar to that followed by Sarkar and Roy. Good pink-coloured transparent crystals were easily obtained from its aqueous solution.

Habit.—Thick prisms of faces (110) and (010) limited by the top faces (001), (011), (20$\bar{1}$) and (111) are generally seen [Fig. 5(*a*)]. It must be noted that the faces (20$\bar{1}$) and (111) are very much diminished in size. Another type consists of plate-like prisms of faces (110), (001), (20$\bar{1}$) and (011) [Fig. 5(*b*)].



$Am_2Ni(BeF_4)_2, 6H_2O$

FIG. 5(*a*) FIG. 5(*b*)

Specific gravity = 1.821.

Axial ratios of $Co(NH_4)_2(BeF_4)_2, 6H_2O$:

$a : b : c = 0.7405 ; 1 : 0.4852 ; \beta = 106° 46'$

Axial ratios of $Co(NH_4)_2(SO_4)_2, 6H_2O$:

$a : b : c = 0.7392 : 1 : 0.4985 ; \beta = 106° 56'$

—	—	Observed	Calculated	Corresponding sulphate
110	$\bar{1}10$	70°35′	70°40′	70°32′
010	110	54°44′	54°40′	54°44′
110	001	76°23′	76°24′	76°15′
111	$\bar{1}11$	38°16′	38°8′	38°40′
111	011	26°30′	26°26′	26°51′
011	001	24°54′	24°35′	25°30′

(c) *Nickel Ammonium Fluoberyllate*

$Ni(NH_4)_2(BeF_4)_2, 6H_2O$.

Class.—Monoclinic prismatic.

Preparation.—The substance was prepared by Sarkar and Ray's method. Bluish-green transparent crystals are obtained from aqueous solution. Faces often become distorted.

Habit.—Similar to cobalt ammonium fluoberyllate, only difference being that (111) faces also appear in this case. Elongated needle-like prisms [Fig. 5(*a*)] as well as short thick prisms [Fig. 5(*b*)] are equally prevalent. The forms usually occurring in these crystals are (110), (011), ($20\bar{1}$), (111), (001), ($\bar{1}11$) and) (010).

Specific gravity = 1.843.

Axial ratios of $Ni(NH_4)_2(BeF_4)_2, 6H_2O$:

$a : b : c = 0.7373 : 1 : 0.4914$; $\beta = 106° 40'$.

Axial ratios of $Ni(NH_4)_2(SO_4)_2, 6H_2O$:

$a : b : c = 0.7370 : 1 : 0.5032$; $\beta = 107° 4'$.

—	—	Observed	Calculated	Corresponding sulphate
110	$\bar{1}10$	70°30′	70°28′	70°20′
110	011	62°42′	62°46	62°14′
$\bar{1}10$	011	88°2′	88°3′	88°6′
110	$20\bar{1}$	52°51	52°58′	52°24′
011	001	25°12	25°13′	25°41′
$\bar{2}01$	001	64°18′	64°12′	65°21′
110	001	76°27′	76°27′	—
010	110	54°44	54°46′	54°50′
110	$11\bar{1}$	58°58′	59°6′	58°29′
$1\bar{1}1$	$\bar{1}10$	87°56′	88°3′	87°56′
001	$\bar{1}11$	44°33′	44°28′	45°24′
011	$\bar{1}11$	34°46′	34°39′	35°20′
001	111	33°46′	33°41′	—

(3) *Sulphato-Fluoberyllates*—

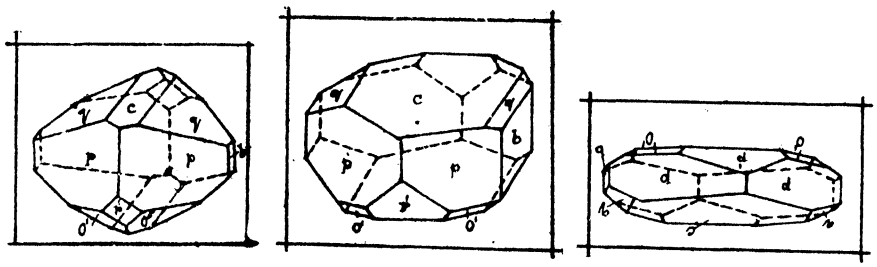
(a) *Zinc Ammonium Sulphate-Fluoberyllate*

$Zn(NH_4)_2BeF_4.SO_4, 6H_2O$.

Class.—Monoclinic Prismatic.

Preparation.—The substance was prepared by Sarkar and Ray's method. It easily crystallises from its aqueous solution at ordinary temperatures as small transparent colourless crystals.

Habit.—The crystals are more or less prismatic, the prisms being of faces (110) [Fig. 6(*a*)]. In the latter case the (001) faces and one of the (010) faces often become strongly developed thus deviating from the prismatic habit [Fig. 6(*b*)]. Occasionally the prism faces remain shorter where the top faces (001) become larger still, so as to give the crystal a thick plate-like nature [Fig. 6(*c*)]. The most common forms are (110), (001), (011), (010), (201) and ($11\bar{1}$).



$Am_2Zn(SO_4BeF_4)$, $6H_2O$

FIG. 6(*a*) FIG. 6(*b*) FIG. 6(*c*)

Specific gravity = 1.843.

Axial ratios $a : b : c = 0.7382 : 1 : 0.4942$; $\beta = 106^\circ 43'$

—	—	Observed	Calculated
110	$\bar{1}10$	70° 32′	70° 32′
010	110	54° 44′	54° 44′
110	001	76° 26′	76° 15′
110	$01\bar{1}$	62° 39′	62° 40′
110	$20\bar{1}$	52° 55′	52° 45′
$1\bar{1}0$	$11\bar{1}$	88° 5′	88° 3′
111	001	44° 34′	44° 39′
111	$\bar{1}11$	49° 15′	49° 20′
201	001	64° 18′	64° 24′
011	001	25° 11′	25° 20′
110	011	88° 3′	88° 0′

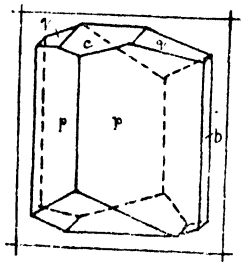
(*b*) *Nickel Potassium Sulphato Fluoberyllate*

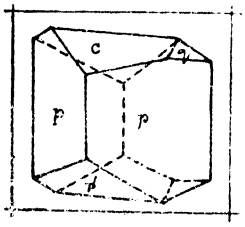
$NiK_2BeF_4.SO_4$, $6H_2O$.

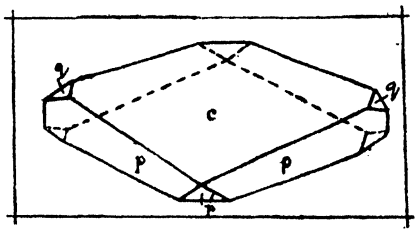
Class.—Monoclinic prismatic.

Preparation.—Same as in the case of zinc-ammonium sulphato-fluoberyllate. Bluish green crystals were easily obtained from its saturated solution in water at ordinary temperatures. The faces of these well-formed crystals have got a marked tendency to become distorted.

Habit.—Prisms of faces (110) with additional faces (010) limited by top face ($20\bar{1}$), (001), (011) are very common [Fig. 7(*a*)]. In some cases only two of the prism faces become highly developed (others remaining reduced) and the crystal assumes a plate-like appearance [Fig. 7(*b*)]. Occasionally the faces (001) and ($20\bar{1}$) become peculiarly magnified while the faces (010) and (011) are completely suppressed. Plates of faces (001) bounded by faces (110), ($20\bar{1}$) and (011) are also met with [Fig. 7(*c*)]







$K_2Ni(SO_4BeF_4)_2 6H_2O$

FIG. 7(*a*) FIG. 7(*b*) FIG. 7(*c*)

Specific gravity = 1.856

Axial ratios $a : b : c = 0.7405 : 1 : 0.5077$; $\beta = 104°44'$

—	—	Observed	Calculated
010	110	54° 22′	54° 24′
110	001	78° 4′	78° 4′
110	011	63° 52′	63° 46′
110	011	86° 1′	85° 56′
110	$20\bar{1}$	52° 15′	52° 4′
$20\bar{1}$	001	63° 39′	63° 51′
011	001	26° 9′	26° 9′

X-RAY MEASUREMENTS

Rotation pictures were taken about the three crystallographic axes with copper $K\alpha$ radiation and a cylindrical camera to determine the cell dimensions of potassium fluoberyllate, rubidium fluoberyllate, thallium fluoberyllate, ammonium fluoberyllate and nickel ammonium fluoberyllate.

The dimensions of the unit cells of the different fluoberyllates are given below in Angstron units :—

Metallic Radical.	Fluoberyllates			Sulphates		
	a	*b*	*c*	*a*	*b*	*c*
Potassium ...	5.63	9.83	7.29	5.73	10.00	7.42
Rubidium ...	5.85	10.13	7.66	5.94	10.39	7.78
Thallium ...	5.87	10.43	7.68			
Ammonium ...	5.89	10 39	7.49	5.95	10.56	7.72
	(5.8	10.2	7.5)	from Hulthgren (1934)		
Nickel Ammonium ...	9.04	12.31	6.04	8.98	12.22	6.10
	$\beta = 106° 40'$			$\beta = 107° 4'$		

The above axial lengths and the monoclinic angles together with the values of the specific gravities gave the following numbers of molecules per unit cell in the different cases.

Substance.		No. of molecules per unit cell.
K_2BeF_4	...	4
Rb_2BeF_4	...	4
Tl_2BeF_4	...	4
$(NH_4)_2BeF_4$	...	4
$Ni(NH_4)(BeF_4)_2, 6H_2O$	...	2

Oscillation photographs were taken about the 'b' and the 'c' axes at intervals of 10° for the correct indexing of the planes. The idices of the spots appearing on the photographs were deciphered by Bernal's method (1927). The following results were obtained with potassium fluoberyllate and nickel ammonium fluoberyllate.

Potassium Fluoberyllate

(1) (h k o) reflections are absent when h + k is odd.

(2) (h o l) reflections are absent when l is odd.

This leads to the space group D_{2h}^{16} Pmcn.

Nickel Ammonium Fluoberyllate

(1) Reflections from (h o l) planes are absent when h is odd.

(2) (o k o) reflections are absent if k is odd.

These halvings correspond to the space group $C_{2h}^{5} P2_1/a$.

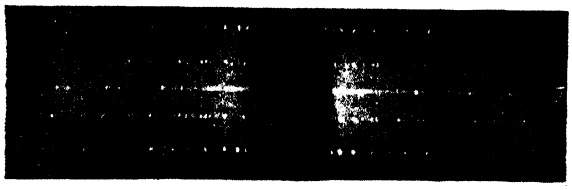
The experimental part of this investigation was carried out at the Physical Laboratory of the Dacca University. The author expresses his thanks to Prof. S. N. Bose for suggesting the problem and providing facilities for the work and to Prof. K. Banerjee for guidance and discussions throughout the progress of the work and to Mr. R. K. Sen for some calculations.

INDIAN ASSOCIATION FOR THE
CULTIVATION OF SCIENCE,
CALCUTTA.

REFERENCES

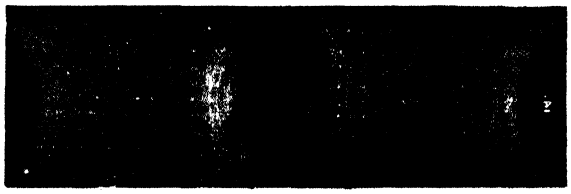
Bernal, J. D. (1927), *Proc. Roy. Soc.*, **113A**, 117.
Hulthgren, R. (1934), *Zeits. f. Krist.*, **88A**, 233.
Koch-Holm, E., and Schonfeldt, N. (1927), *Wiss. Veroff. Siemens Konz.*, **6**, 177.
Sarkar, P. B., and Ray, N. (1929), *J. Ind. Chem. Soc.*, **6**, 987.

A



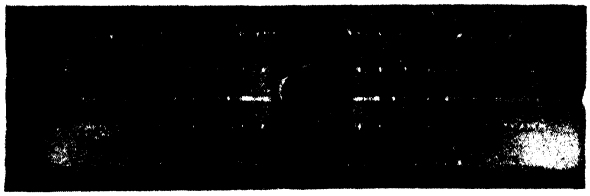
Rotation Photograph of Rubidium Fluoberyllate about a—axis.

B



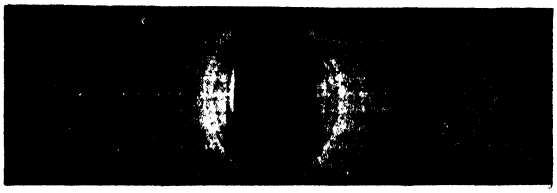
Rotation Photograph of Thallium Fluoberyllate about b—axis.

C



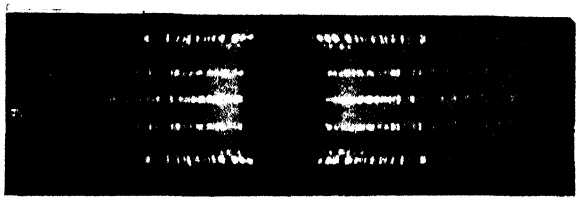
Rotation Photograph of Potassium Fluoberyllate about a—axis.

D



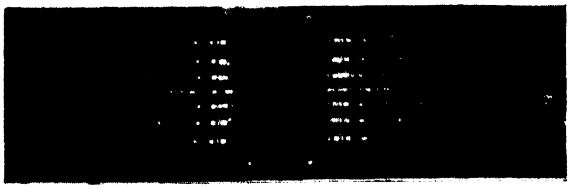
Rotation Photograph of Potassium Fluoberyllate about b—axis.

E



Rotation Photograph of Ammonium Fluoberyllate about a—axis.

F



Rotation Photograph of Ammonium Fluoberyllate about b—axis.